

**AD-A280 829**



①

**OFFICE OF NAVAL RESEARCH**

**CONTRACT N00014-94-1-0101**

**R&T Code 31321075**

**Technical Report No. 22**

**RADICAL POLYMERIZATION OF VINYL ACETATE IN THE PRESENCE  
OF TRIALKYL PHOSPHITES**

by

**Dorota Greszta, Daniela Mardare, Krzysztof Matyjaszewski**

Published

in the

**ACS Polym. Preprints, 35(1), 466 (1994)**

**Carnegie Mellon University  
Department of Chemistry  
4400 Fifth Avenue  
Pittsburgh, PA 15213**

**DTIC QUALITY INSPECTED 2**

**June 30, 1994**

**Reproduction in whole or in part is permitted for any purpose of the United States Government**

**This document has been approved for public release and sale;  
its distribution is unlimited.**

**94-20043**



**94 6 29 085**

REPORT DOCUMENTATION PAGE			GPO 554-754-01	
<small>           This report is published for the use of information systems and is not to be used for other purposes. It is not to be used for the purpose of making a copy of the report for other purposes. It is not to be used for the purpose of making a copy of the report for other purposes. It is not to be used for the purpose of making a copy of the report for other purposes.         </small>				
1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE June 30, 1994	3. REPORT TYPE AND DATES COVERED Technical Report # 22	
4. TITLE AND SUBTITLE Radical Polymerization of Vinyl Acetate In The Presence of Trialkyl Phosphites			5. FUNDING NUMBERS N00014-94-1-0101	
6. AUTHOR(S) Krzysztof Matyjaszewski, Dorota Greszta, Daniela Mardare				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Carnegie Mellon University Department of Chemistry 4400 Fifth Avenue Pittsburgh, PA 15213			8. PERFORMING ORGANIZATION REPORT NUMBER N00014-94-1-0101	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Department of the Navy Office of Naval Research 800 North Quincy Street Arlington, VA 22217-5000			10. SPONSORING/MONITORING AGENCY REPORT NUMBER Technical Report #22	
11. SUPPLEMENTARY NOTES ACS Polym. Preprints, <u>35(1)</u> , 466 (1994)				
12a. DISTRIBUTION/AVAILABILITY STATEMENT			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words)  <p>Radical polymerization of vinyl acetate initiated by BPO in the presence of different phosphites was studied. As it was observed, trialkylphosphites enhance polymerization rates. The molecular weights of polymers are affected by the initiator concentration and can be adjusted to higher or lower values. Polydispersities do not change with conversion and are lower than for PVAc obtained with BPO as an initiator ( usually <math>M_w/M_n = 1.6</math> to <math>1.7</math> for BPO/TFEP as an initiating system.). The presence of pentavalent phosphorous atoms in the BPO/TFEP system as well as in polymer obtained with that system was revealed by <math>^{31}\text{P}</math>-NMR spectroscopy.</p>				
14. SUBJECT TERMS			15. NUMBER OF PAGES	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Classified	18. SECURITY CLASSIFICATION OF THIS PAGE Classified	19. SECURITY CLASSIFICATION OF ABSTRACT Classified	20. LIMITATION OF ABSTRACT UL	

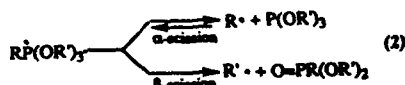
# RADICAL POLYMERIZATION OF VINYL ACETATE IN THE PRESENCE OF TRIALKYL PHOSPHITES

Dorota Greszta, Daniela Mardare and Krzysztof Matyjaszewski\*

Carnegie Mellon University  
Department of Chemistry  
4400 Fifth Avenue  
Pittsburgh, PA, 15213

## Introduction

Reactions involving free radicals and trivalent phosphorus compounds such as alkyl (aryl) phosphines or phosphites have been intensively studied in recent years<sup>1</sup>. The reaction products were often identified as phosphoranyl radicals, which may undergo subsequent  $\alpha$  or  $\beta$ -scissions (eq. 1,2)<sup>2</sup>:



The former reaction is usually an opposite reaction to the formation of phosphoranyl radical, whereas the latter one is the oxidation process which leads to the formation of P=O bonds, like in Arbuzov rearrangement. There are a few examples of radical polymerization of some acrylic monomers (methyl methacrylate, acrylonitrile) in the presence of trivalent phosphorus compounds (phosphines, phosphites)<sup>3,4</sup>. A monomer-PR<sub>3</sub> complexation affects the polymerization kinetics, whereas molecular weights and polydispersities are not influenced by the initiator/phosphorus ratios.

In this paper we report on the radical polymerization of vinyl acetate (VAc) initiated by benzoyl peroxide (BPO) in the presence of phosphites or phosphates. Molecular weights and polydispersities of poly(vinyl acetate) prepared by initiation with (BPO)/tris(2,2,2-trifluoroethyl)phosphite system do not vary with conversion. In contrast, when BPO alone was used as initiator, a strong decrease in molecular weights with conversion was noticed, as well as a significant increase in polydispersities ( $M_w/M_n = 1.4$  to 1.95). Higher concentrations of initiator lead to lower molecular weights, independently of the initiator/phosphite molar ratios.

## Results and Discussion

Polymerization rates increase in the presence of tris(2,2,2-trifluoroethyl)phosphite (TFEP). Figure 1 presents time-conversion plots in semilogarithmic coordinates for polymerization of VAc, initiated by TFEP/BPO (1.5/1) and BPO alone, at the same concentration of peroxide (0.025M). The kinetic plots obtained in the presence of phosphite are linear, indicating that the concentration of the growing radicals does not vary during polymerization.

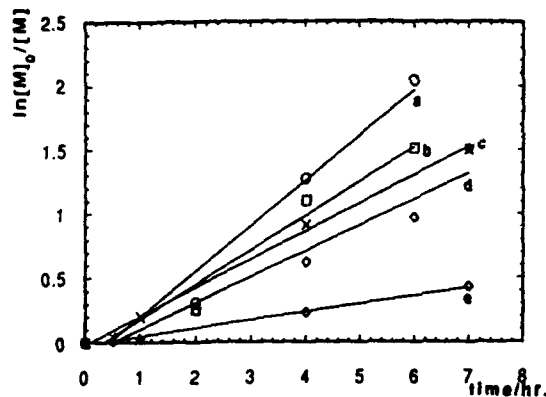


Figure 1. Time-conversion plots in semilogarithmic coordinates in polymerization of VAc initiated by BPO/TFEP(1/1.5) and BPO alone, [VAc]<sub>0</sub> = 5.4M, benzene, 60°C, [BPO]<sub>0</sub>/[TFEP]<sub>0</sub> = 1:1.5, (a) [BPO]<sub>0</sub> = 0.11M, (b) [BPO]<sub>0</sub> = 0.08M, (c) [BPO]<sub>0</sub> = 0.05M, (d) [BPO]<sub>0</sub> = 0.025M, (e) [BPO]<sub>0</sub> = 0.025M, no TFEP

Figure 2 presents effect of added TFEP on the variation of molecular weights with conversion for polymerization of VAc initiated by BPO at 60°C. In polymerization initiated by BPO alone, molecular weights decrease with conversion. This can be ascribed to the much stronger decrease of the propagation rate in comparison with the initiation rate. Polymerization degrees, defined by the ratio of the corresponding rates (assuming no contribution of transfer) decreases gradually with conversion. In contrast, polymerization in the presence of phosphites provides constant value of the molecular weight during entire polymerization process. Molecular weights are, however, affected by the concentration of phosphite/BPO initiating system. Higher molecular weights are observed at lower initiator concentration.

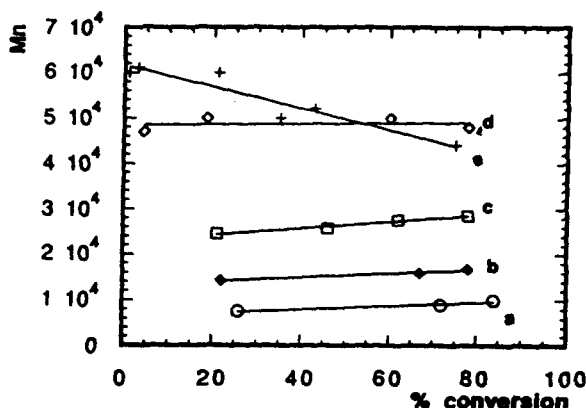


Figure 2.  $M_n$ -conversion dependence in polymerization of VAc initiated by TFEP/BPO ([VAc]<sub>0</sub> = 5.4M, benzene, 60°C, [BPO]<sub>0</sub>/[TFEP]<sub>0</sub> = 1:1.5, (a) [BPO]<sub>0</sub> = 0.11M, (b) [BPO]<sub>0</sub> = 0.08M, (c) [BPO]<sub>0</sub> = 0.05M, (d) [BPO]<sub>0</sub> = 0.025M, (e) [BPO]<sub>0</sub> = 0.025M, no TFEP

Variation of molecular weights with conversion for the initiation with BPO alone leads to the increase of polydispersities. Initially, low values in the range of  $M_w/M_n = 1.5$  may indicate termination by coupling, as expected for polymerization of vinyl acetate<sup>5</sup>. Polydispersity increases strongly with conversion (to  $M_w/M_n > 2$ ), because molecular weights decrease due to the reduction of the ratio rate of propagation/rate of initiation. Surprisingly, polydispersities in the presence of phosphite do not change during entire polymerization ( $M_w/M_n = 1.6$  to 1.7), as shown in Figure 3

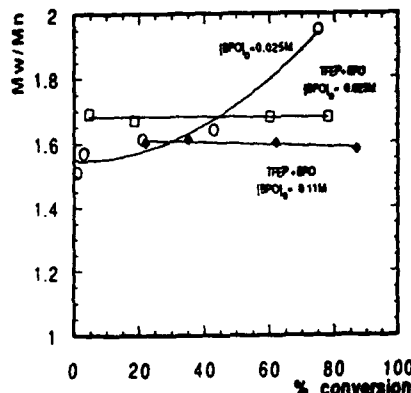


Figure 3.  $M_w/M_n$  - conversion dependence in polymerization of VAc initiated by TFEP/BPO (1.5/1)

Dist

Avail and/or  
Special

A-1

Structure of phosphites strongly affect polymerization of vinyl acetate initiated by BPO. Table 1 shows the influence of different phosphites on polymerization of VAc in benzene at 60°C.

Table 1  
Effect of the Structure of Phosphites on Polymerization of Vinyl Acetate in Benzene at 60°C a)

Phosphite	$M_n$	$M_w/M_n$	Conversion, %
$(CH_3O)_3P$	99,000	1.55	18
$(n-C_4H_9O)_3P$	84,000	1.56	5
$(i-C_3H_7O)_3P$	-	-	< 0.5
$(CF_3CH_2O)_3P^{b)}$	63,000	1.39	85

a)  $[P(OR)_3]_0/[BPO]_0 = 1.5/1$ ,  $[BPO]_0 = 0.025$  mol/L,  $[VAc]_0 = 7$  mol/L, 24 hours  
b) time = 6 hours

Polymerization rates are probably affected by both steric and electronic factors. Rates are strongly reduced by the increase of the size of alkyl group in the phosphite (Me < Bu < iPr). However, trifluoroethyl group has the intermediate size but provides the fastest polymerization. This could be ascribed to the electronic effects.

Replacement of a trivalent trimethyl phosphite,  $(CH_3O)_3P$ , with a pentavalent trimethyl phosphate  $(CH_3O)_3P=O$ , leads to a strong increase of the rate and polydispersity and change of the molecular weight (after 24 hours - 83% conversion;  $M_n = 27,000$ ;  $M_w/M_n = 2.72$ ). These data are very similar to the polymerization initiated by BPO alone. This may indicate that phosphates have very small effect on polymerization of vinyl acetate, in contrast to phosphites.

In order to get a deeper insight into the nature of the initiating system, the reaction of TFEP with BPO (1.5/1) was followed by  $^{31}P$ -NMR. At room temperature after 0.5 hours no reaction was observed and only the original signal of TFEP at 139 ppm was detected. When the reaction temperature was increased to 60°C, after 0.5 hours a new signal of pentavalent phosphorous ( $\delta = -2.6$  ppm) was found. Figure 4 shows the  $^{31}P$ -NMR spectrum of this reaction mixture.

